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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Method for Gold Recovery Using Chlorine Dioxide Solution

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ABSTRACT OF DISCLOSURE

Sulfide ores or those containing carbonaceous material are reacted with chlorine dioxide to release a  
5 metal, particularly gold, therefrom for recovery.

1           The embodiments of the invention in which an exclusive  
2 property or privilege is claimed are defined as follows:

3           1. A method for treating sulfide ores or ores containing  
4 carbonaceous materials for the recovering of a metal therefrom  
5 comprising reacting the ore with chlorine dioxide thereby to  
6 release the metal.

7  
8           2. The method of Claim 1, wherein the chlorine dioxide is  
9 in a water solution further comprising grinding the ore and  
10 mixing it with water to form the slurry, and wherein the  
11 reacting step comprises mixing the slurry with the chlorine  
12 dioxide solution.

13  
14           3. The method of Claim 2, wherein the ore is ground to an  
15 average size of 100-400 mesh and the water slurry is formed by  
16 mixing water with 10-65% by weight of the ground ore; and the  
17 chlorine dioxide water solution is formed by dissolving at  
18 least 0.05% by weight chlorine dioxide in water.

19  
20           4. The method of Claim 3, wherein at least 1 kg of  
21 chlorine dioxide per metric ton of ore in the slurry, is  
22 reacted with the slurry.

23  
24           5. The method of Claim 1, further comprising recovering  
25 the released metal.

26  
27           6. The method of Claim 5, wherein the recovering of the  
28 released metal comprises solubilizing the metal and dissolving  
29 it into solution, and thereafter separating the metal from the  
30 solution.

31  
32           7. The method of Claim 6, wherein the chlorine dioxide  
33 solubilizes the metal.

34  
35           8. The method of Claim 7, wherein the metal is gold.

1           9. The method of Claim 1, wherein the chlorine dioxide is  
2 in a water solution, further comprising crushing the ore and  
3 piling it into a heap; and wherein the reacting step comprises  
4 percolating the chlorine dioxide solution through the heap.  
5

6           10. The method of Claim 9, wherein the ore is crushed to  
7 about 1/4 inch - 6 inches.  
8

9           11. The method of Claim 9, wherein the metal is  
10 solubilized by chlorine dioxide solution, further comprising  
11 collecting the solution percolated through the heap and  
12 recovering dissolved metal therefrom.  
13

14           12. The method of Claim 11, wherein the metal is gold.  
15

16           13. A heap leach method for treating ores for recovering  
17 of metals, wherein the ore is crushed and piled in a prepared  
18 surface, and wherein a leaching agent is percolated through the  
19 pile and collected for recovery of the metals dissolved therein  
20 the improvement wherein sulfide ores as well as oxide ores can  
21 be treated and comprising using as the leaching agent a  
22 solution of chlorine dioxide.  
23

24           14. A method of leaching a metal comprising reacting the  
25 metal with chlorine dioxide, in water solution.  
26

27           15. The method of Claim 14, wherein the metal is  
28 contained in an ore, comprising crushing or grinding the ore  
29 and contacting the ore with chlorine dioxide, in water  
30 solution.  
31

32           16. The method of Claim 15, wherein the chlorine dioxide  
33 is dissolved in water at a rate of at least 0.05% chlorine  
34 dioxide by weight, and thereafter the chlorine dioxide solution  
35 is reacted with the ore.

A METHOD FOR GOLD RECOVERY USING CHLORINE DIOXIDE SOLUTION

BACKGROUND OF THE INVENTION

The present invention is directed to the recovery of gold, silver and other oxidizable metals from naturally occurring sulfide and oxide ores. The present invention is particularly useful in ores containing refractory sulfides, carbonaceous matter, or which are difficult to process by the methods of prior art.

The present invention replaces the current practice of using sodium cyanide solutions with an ecologically and economically more advantageous method.

Although the present invention is expected to have wide applicability in the processing of metal ores in view of its ecological and economic advantages, initially it is expected to have greatest impact on the way refractory sulfide-containing ores are processed for recovery of gold and silver. Furthermore, it is easily envisioned that the current invention can be used to treat ores containing oxidizable or carbonaceous impurities that interfere with the current practice of leaching with a sodium cyanide solution. These are primarily oxide ores.

Current practice in the mining industry for the extraction of gold and silver from refractory sulfide ores is a two step process. The first step uses thermal roasting, pressure oxidation, or bacterial oxidation to chemically break down the sulfides in ground ore slurries and concentrates. This pretreatment step oxidizes sulfide impurities to sulfur

1 dioxide and/or sulfates exposing the microscopic gold  
2 particles for the cyanide leach step that follows. When  
3 thermal roasting or pressure oxidation is used, the reaction is  
4 generally stoichiometric for the sulfide impurities in the ore.  
5 Chlorination is commonly used in current practice to remove  
6 carbonaceous impurities from oxide ores. The usage of  
7 chlorine is sufficient to remove most, or all, of the  
8 carbonaceous impurities.

9  
10 The second step, leaching the pretreated ore with a dilute  
11 sodium cyanide solution, converts the gold into a soluble gold  
12 cyanide complex from which it can be recovered by any one of a  
13 number of commercially practiced processes including  
14 precipitation, carbon adsorption, and electrowinning.

15  
16 In one embodiment of prior art, a sulfide ore slurry is  
17 placed in a large autoclave where steam, oxygen, and sometimes  
18 sulfuric acid is forced through the ore to oxidize sulfide  
19 impurities. This method called "pressure oxidation" may  
20 require several hours of processing time. The oxidation  
21 pretreatment is followed by neutralization with lime, then by  
22 addition of a basic solution of sodium cyanide as the primary  
23 leaching agent. The resulting soluble gold cyanide complex is  
24 treated by carbon adsorption, precipitation, or electrowinning  
25 for gold and silver recovery. This method does not release the  
26 copper, antimony, and base metals that may be present.

27  
28 In a modification of this method, oxide ore containing  
29 little or no sulfide impurity is piled in a mound ("heap") up  
30 to 200 feet high, in an area which can be many acres in size.  
31 Sodium cyanide solution is then distributed evenly over the  
32 heap during a period of weeks to months from sprinklers or  
33 emitters, not unlike lawn sprinklers or emitters. The sodium  
34 cyanide solution percolates down through the heap, dissolving  
35 the gold as a gold cyanide complex, and is collected in usually

1 open lined ponds. Gold is then recovered by the usual  
2 processes discussed above. This method is called a "heap  
3 leach" process. Although it is an economical one-step leaching  
4 process for oxide ores, the open cyanide ponds involve a degree  
5 of environmental and ecological risk.

6  
7 With the changing view concerning ecology, the degree of  
8 risk in prior art methods can be unacceptable especially in  
9 ecologically sensitive areas. That is, the use of pressure  
10 oxidation or thermal roasting followed by a cyanide leach  
11 method is considered to be disadvantageous because of the risk  
12 of cyanide contamination and sulfur dioxide emissions.  
13 Furthermore, from an economic point of view, it is difficult to  
14 attain a high recovery of the gold (which is entrapped usually  
15 in the form of microscopic particles) from refractory sulfide  
16 ores using current technology. Often, recoveries of 70 to 80%  
17 are considered excellent, especially for low quality refractory  
18 sulfide ores. Many low quality ores, sulfide and oxide ores  
19 included, cannot be economically processed at such low recovery  
20 levels. Coupled with the difficulties of treating or disposing  
21 of cyanide containing tailings, especially in ecologically  
22 sensitive areas, it is clear that new methods of gold recovery  
23 are desirable to replace the known cyanide method.

24  
25 One embodiment of the present invention uses a one-step  
26 leaching process employing chlorine dioxide to free the  
27 entrapped gold, silver, and other metals, and complex the  
28 metals into solution. It can be practiced in relatively small  
29 plants using static mixers, agitated tanks, or, possibly, vat  
30 or heap leach methods. Gold is converted into a soluble gold  
31 chloride complex which can be recovered using ion exchange  
32 resin, precipitation, electrowinning, or other methods for the  
33 removal of water and salting out of gold.

1        Although an exhaustive study has not been made to fully  
2 characterize the manner in which the present invention  
3 operates, it is believed that the chlorine dioxide attacks the  
4 sulfide ore stress fractures and fissures to break the sulfide  
5 structure into small and possibly colloidal size particles.  
6 This action releases microscopic particles of gold which are  
7 entrapped within the sulfide structure for further reaction  
8 with chlorine dioxide to form a soluble gold chloride complex.  
9 Other, less noble metals such as copper, antimony, and other  
10 base metals contained in the ore form soluble chlorides.

11  
12        The only metal recovery process of which applicants are  
13 aware which uses chlorine dioxide is a process for vanadium  
14 recovery described in British Patent Application GB 2155917.  
15 The method described therein involves the removal and recovery  
16 of vanadium, from a vanadium bearing material, using a caustic  
17 solution as the leaching agent. This is basically different  
18 from the present invention which uses chlorine dioxide as a  
19 leaching agent.

20  
21        To enhance the leaching process, the British patent  
22 application teaches the use of a "leaching promotor" in the  
23 caustic leaching solution. The leaching promotor is selected  
24 from the group consisting of an ionic form of vanadium;  
25 hypochlorites of sodium, calcium and potassium; peroxides;  
26 chlorine dioxide and mixtures thereof. By contrast, as will be  
27 discussed below, the present invention involves contacting the  
28 ore with a chlorine dioxide solution to free gold and silver  
29 from a sulfide or oxide ore matrix and to oxidize gold and  
30 silver to a soluble oxidation state. The result is a solution  
31 which is neutral or acidic. The chlorine dioxide is the  
32 leaching agent. A caustic leaching agent is not used. Thus,  
33 the process is substantially different in principle of  
34 operation as well as in practice.

35



1  
2 **SUMMARY**

3 A first embodiment of the present invention is a one-step  
4 process for treating ores for the recovery of metals which can  
5 be leached with chlorine dioxide. In particular, the present  
6 invention provides a method for recovering gold and silver from  
7 ores containing carbonaceous materials and from sulfide ores.  
8 In particular the invention can be applied to low quality,  
9 refractory sulfide ores without the need for pretreatment, or  
10 the use of ecologically undesirable cyanide.

11  
12 As will be evident from the detailed description, the  
13 first embodiment of the present invention is useful for  
14 leaching a variety of metals which are solubilized with  
15 chlorine dioxide. In addition chlorine dioxide is also highly  
16 effective for releasing metals from sulfide ores in general.

17  
18 In accordance with the present invention, the ores are  
19 crushed or ground, and in one embodiment, a slurry in water is  
20 formed from the ores. Chlorine dioxide, normally in aqueous  
21 solution, is then passed through the ore slurry in a reaction  
22 which appears to be complete in less than thirty minutes at  
23 room temperature. The gold (and other metals), now in the form  
24 of a soluble gold chloride complex, can be separated from the  
25 spent ore slurry by decantation or other known mechanical  
26 processes. In another embodiment chlorine gas is passed  
27 through the soluble gold chloride solution to maintain an  
28 acidic solution and reduce the usage of chlorine dioxide which  
29 is more expensive. This practice can also contribute to high  
30 gold recovery values.

31  
32 The metal is then recovered from solution by a known  
33 method such as ion exchange, carbon adsorption, electrowinning  
34 or precipitation.

35

1       Because of the high efficiency with which chlorine dioxide  
2 breaks the sulfide matrix, it can be used to advantage in  
3 releasing metals other than gold and silver. A broad range of  
4 metals can be released by chlorine dioxide for recovery by  
5 other methods. This single step process can also be applied to  
6 heap leach operations by substituting chlorine dioxide solution  
7 for the present practice of using sodium cyanide solution.  
8

9       As compared with the prior art method of treating  
10 refractory sulfide ores to release gold and solubilize it for  
11 recovery, the present invention results in consistently high  
12 yields. More importantly, the present invention is a single  
13 step process while the prior art requires a pretreatment step  
14 followed by a cyanide step in order to solubilize the gold.  
15

16       The prior art single step, heap leach process involves  
17 large piles of ore over which cyanide solution is sprayed or  
18 emitted under ecologically difficult conditions and is not  
19 successful with refractory sulfide ores. The present invention  
20 does not use cyanide and is therefore ecologically preferable:  
21 chlorine dioxide has a history of usefulness for treatment of  
22 municipal water supplies and has been found ecologically safe.  
23

24       From an economic point of view, the present invention can  
25 provide high processing efficiencies with relatively small  
26 plants because of the short ore contact time required, and can  
27 eliminate the environmental and ecological risk associated with  
28 cyanide containing ponds and tailings piles.  
29

#### 30       DETAILED DESCRIPTION OF THE INVENTION

31       The present invention has application in the recovery of  
32 gold, silver, and other metals forming soluble chlorides from  
33 high sulfide, ores. It also has applicability for recovering  
34 other metals from ores where the cyanide process or other  
35 process using ecologically unacceptable agents are now

1 practiced. Furthermore, it can be used to release metals from  
2 ores to increase recovery yields of metals in processes wherein  
3 chlorine dioxide is not presently used as the leaching agent.  
4

5 By way of example, the processing of gold ore will be  
6 described in detail.  
7

8 Preparatory to the recovery of metals in ores, it is usual  
9 to crush or to grind the ores for handling ease and to expose  
10 the metals. Thus, depending on the process to be applied, ore  
11 is crushed or is further processed by grinding.  
12

13 Typical ore crushing equipment now used in treating ores,  
14 can crush ore down to about 1/4 inch pieces although much  
15 larger pieces are usual. Crushed ore is used for heap leaching  
16 processes where rapid reaction or leaching times are not an  
17 important factor. Heap leaching processes, by their nature,  
18 can tolerate a wide range of ore sizes. However, the larger  
19 the average size, the longer the leaching time required.  
20

21 Furthermore, the usual heap leaching processes, which do  
22 not use a pretreatment step to free metals from the ores, such  
23 as chlorination, oxidation and/or roasting, cannot be  
24 successfully applied to refractory sulfide ores.  
25

26 Vat leaching processes can utilize a two step treatment  
27 and are applicable to refractory sulfide ores. For the vat-  
28 leach process where rapid reaction times are important, the ore  
29 must be ground. Typical grinding equipment now in use in the  
30 field will grind ore down to about 400 mesh size. 100 mesh to  
31 400 mesh grinding is normally accomplished without special  
32 procedures and this range is suitable for pumpable water  
33 slurries.  
34  
35

1       The present invention leaching method can be applied to  
2 heap-leach or vat-leach analogous processes.  
3

4       The heap-leach method can be essentially the same as it is  
5 now practiced. The improvement is to substitute a chlorine  
6 dioxide solution for the cyanide leaching solution normally  
7 used. For economic reasons, the chlorine dioxide solution,  
8 would normally be at the low end of useful concentration,  
9 normally 0.01% to 1% and preferably 0.05% to 0.3%.

10  
11       A vat-leach analogous process can be practiced in a vat or  
12 in flow mixers or other smaller size equipment (compared to the  
13 huge piles used in heap-leaching). The usual grinding  
14 equipment can be used as a 100 to 400 mesh slurry will react  
15 sufficiently quickly for commercial operations. Although  
16 grinding to a smaller size is also suitable, the current cost  
17 of doing so does not provide any corresponding advantage.  
18 Grinding to a significantly larger size than the 100 mesh would  
19 also work; however, as the size of the ore increases, the  
20 reaction time required for high gold recovery also increases.  
21 With too large an ore size it may not be possible to accomplish  
22 the high recovery rates, which are possible even with low  
23 quality ores using the present invention. Higher  
24 concentrations of chlorine dioxide can be used and  
25 concentrations up to a saturated or supersaturated solution are  
26 contemplated. Lower concentrations of chlorine dioxide can be  
27 used but reaction times will be slower.  
28

29       A slurry may be formed by mixing the ground ore with  
30 water. Typically a 10% to 65% by weight slurry is used.  
31 Although higher solid concentrations can be used, pumping  
32 difficulties can be encountered. Using a slurry with much less  
33 than 10% solids results in dilution of the chlorine dioxide  
34 solution.  
35

1        In small scale studies, it has been found that the  
2 reaction goes essentially to completion within about one minute  
3 or less. For commercial, large-scale processing, it is  
4 expected that reaction times of about 30 minutes or less will  
5 be used to insure that all of the slurry has had time to come  
6 in contact with the chlorine dioxide, except in heap leach  
7 operations where the volume of ore to be treated and larger  
8 ore pieces require longer times. However, vat reactors with  
9 residence times of less than 30 minutes are easily envisioned.  
10 Static mixers can be used to obtain the necessary contact  
11 between the ore and chlorine dioxide, although agitated mixing  
12 equipment normally available in commercial installations is  
13 suitable. The reaction will proceed even in a pipe through  
14 which the slurry is pumped. It is only necessary that the  
15 chlorine dioxide solution come into intimate contact with the  
16 gold ore.

17        After treatment with chlorine dioxide, the water solution  
18 of gold and silver chloride complex is separated from the spent  
19 ore and the gold and silver is recovered therefrom.  
20 Electrowinning or other methods can be used, including  
21 precipitation and ion exchange. If recovery by ion-exchange  
22 resin is contemplated, chlorine gas can be percolated through  
23 the gold bearing solution to adjust the pH and extend the  
24 useful life of the ion exchange resin. Recoveries of 70% to  
25 80% are usual even with low quality ores.

#### 26 27 EXAMPLES OF PREFERRED EMBODIMENTS

28        A wide variety of chlorine dioxide-generating processes  
29 may be employed in the present invention. One class of such  
30 processes is based on sodium chlorate, which is reacted with a  
31 reducing agent in the presence of a strong mineral acid, such  
32 as sulfuric acid, hydrochloric acid and phosphoric acid.  
33 Another class of such processes is based on sodium chlorite,  
34 which is reacted with oxidizing agent and/or a strong mineral  
35 acid. Combinations of sodium chlorate and sodium chlorite also

1 may be employed.

2  
3 Specific examples of combinations of reactants which may  
4 be employed are (a) sodium chlorate, sodium chloride and  
5 sulfuric acid, (b) sodium chlorate and hydrochloric acid, (c)  
6 sodium chlorate, sodium chlorite, sodium chloride and sulfuric  
7 acid, (d) sodium chlorate, sodium chlorite and hydrochloric  
8 acid, (e) sodium chlorate, sulphur dioxide and sulfuric acid,  
9 (f) sodium chlorate, methanol and sulfuric acid, (g) sodium  
10 chlorite and chlorine, (h) sodium chlorite and hydrochloric  
11 acid and/or sulfuric acid, (i) sodium chlorite, oxidizing gas  
12 and sulfuric acid, (j) sodium chlorate, sodium chloride,  
13 hydrogen peroxide and/or methanol and sulfuric acid, (k)  
14 sodium chlorite, sodium hypochlorite and hydrochloric acid  
15 and/or sulfuric acid, and (l) sodium chlorate, glucose and  
16 sulfuric acid. Other suitable combinations of reactants also  
17 may be employed.

18  
19 According to the practice of the present invention,  
20 chlorine dioxide solution can be generated on-site by the  
21 process and apparatus described in United States patent numbers  
22 4,292,292, "Chlorine Dioxide Generation Process"; 4,247,531,  
23 "Chlorine Dioxide Generation Apparatus and Process"; and  
24 4,590,057 "Process for the Generation of Chlorine dioxide". In  
25 general the precursor reactants (chlorine and sodium chlorite  
26 or sodium hypochlorite, hydrochloric acid, and sodium chlorite)  
27 are vacuum educted into the generator reaction chamber where  
28 gaseous chlorine dioxide is formed according to the following  
29 reactions:

30

31  $2\text{NaClO}_2 + \text{Cl}_2 \rightarrow 2\text{ClO}_2 + 2\text{NaCl}$  (Two Chemical Process)

32  $2\text{NaClO}_2 + \text{NaOCl} + 2\text{HCl} \rightarrow 2\text{ClO}_2 + 3\text{NaCl} + \text{H}_2\text{O}$  (Three Chemical Process)

33

34 The gaseous chlorine dioxide produced herein is  
35 immediately educted into a process water stream resulting in a

1 chlorine dioxide solution of up to 10 gms. per liter  
2 concentration. Although a wide concentration range can be  
3 used, the preferred range of chlorine dioxide concentration for  
4 the present invention is 0.05% to the saturation point of  
5 chlorine dioxide in water.  
6

7 Example 1. A high sulfide ore containing 10 gms/M ton  
8 gold and recoverable quantities of silver, platinum, copper,  
9 and base metals in a matrix containing 5.5%  $S^0$  as sulfides and  
10 0.8%  $C_2MgCO_3$  is treated with 5.5 kg/M ton chlorine dioxide for  
11 five minutes contact time. The gold is recovered by ion  
12 exchange using Rohm & Haas Amberlite IRA-900C resin. Percent  
13 gold recovery by fire assay is 71%.  
14

15 Example 2. Same ore as in example 1. treated with 2.5  
16 kg/M ton chlorine dioxide plus 1.75 kg/M ton chlorine for five  
17 minutes contact time. The gold is recovered and analyzed as in  
18 example 1. gold recovery percentage is 86%.  
19

20 Example 3. Same ore and conditions as example 2. with  
21 thirty minutes of contact time. 93% gold recovery is attained.  
22

23 Example 4. An oxide ore containing less than 0.25%  $S^0$  as  
24 sulfides and 8 gms/M ton gold is treated with 2.5 kg/M ton  
25 chlorine dioxide and 1.75 kg/M ton chlorine for 30 minutes  
26 contact time. The gold is recovered by ion exchange using Rohm  
27 & Haas Amberlite IRA-900C resin and analyzed by fire assay.  
28 The gold recovery rate is 100%.  
29

30 Although the present invention appears similar to the  
31 pretreatment accomplished in the prior art, it is clear that  
32 there are significant differences both in principle and in  
33 practice. The most significant difference is, of course, that  
34 the prior art requires a cyanidization step to solubilize the  
35 gold. This prior art second step must be accomplished in a

1 basic solution of approximately pH 11 to avoid the release of  
2 highly toxic cyanide gas.  
3

4 Another difference is that, when pretreatment is by  
5 thermal roasting or pressure oxidation, the reaction is  
6 stoichiometric for the conversion of sulfide to sulfate whereas  
7 the present invention, using chlorine dioxide, is not a  
8 stoichiometric reaction. In a heap leaching embodiment, the  
9 use of chlorine dioxide provides high yields without the use of  
10 cyanide. Also, refractory sulfide ores can be successfully  
11 treated.  
12

13 The above is illustrative of the preferred embodiment of  
14 the present invention. Because of the value of gold, most of  
15 the work done to date is with gold and with silver which is a  
16 usual precious metal in coexistence with gold, in the ores  
17 normally processed. However, as is readily realized, the  
18 breaking of the sulfide ore matrix to release metals can be  
19 used to release any metals contained therein. Therefore, the  
20 use of  $\text{ClO}_2$  to release metals from sulfide ores is not limited  
21 to gold and silver metals.  
22

23 The present invention, because of its sound environmental  
24 and ecological basis, is a highly useful process for recovery  
25 of metals from oxide or sulfide ores where present technology  
26 cannot be practiced because of environmental and legal  
27 restrictions.  
28  
29  
30  
31  
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34  
35